Electrochemical Oxidation of Hexasulfonated Calix[6]arenes: Surface modification and sensitive detection

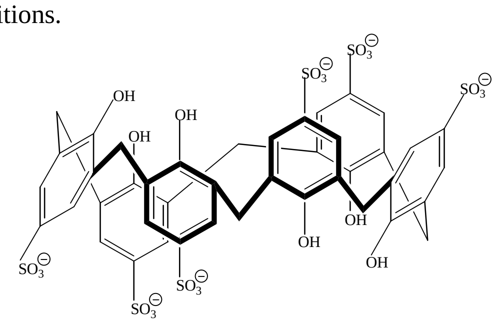
Alain Pailleret[a] and Damien W. M. Arrigan[a,b]
[a]Institute for Materials Research & Chemistry, Cockcroft Building, University of Salford, Salford M5 4WT, United Kingdom
[b]National Microelectronics Research Centre, University College, Cork, Ireland. damien.arrigan@nmrc.ie

Due to their conformational and structural flexibility, calixarenes have received much attention as the basis for molecular and ionic recognition [1,2]. Shinkai and co-workers introduced the water-soluble sulfonated calixarenes as a means of applying these compounds in aqueous-phase applications as uranophiles, binding molecules for ferrocene and cobalticinium derivatives and ammonium cations and also as doping anions in conducting polymers for example [3]. Moreover, these compounds can be further derivatised to introduce additional binding functionality. We show here that electrochemistry of hexasulfonated calix[6]arenes **1** allow not only their electrodeposition on glassy carbon electrodes [4] but also their rather very sensitive electrochemical detection.

First, we show that the first pH dependant oxidation step of one or several of the 2,4,6-trisubstituted phenol moieties of the hexasulfonated calix[6]arene **1** allow their electrodeposition from aqueous solution onto glassy carbon electrodes in the 2 to 10 pH range (Figure 1). This has been confirmed from the dramatic changes of the electrochemistry of the $Fe(CN)_6^{3-/4-}$ redox probe while the electrochemistry of $Ru(NH_3)_6^{3+/2+}$ remains unchanged at these calixarene modified electrodes.

Second, we show that at 13 pH, this first oxidation step is revealed by a narrower, sharper and more intense peak appearing at a less positive potential as the scan rate is lower in cyclic voltammetry, suggesting a surface controlled immobilisation process. Such process has actually been confirmed and characterised using adsorptive stripping voltammetry (Figure 2). The variations of the resulting oxidation peak currents that has been investigated as a function of the deposition potential (Figure 3), the deposition time, the hexasulfonate calix[6]arene concentration and the scan rate seem to lead to a LOD close to micromolar concentrations for hexasulfonated calix[6]arenes under optimized conditions.

1



References :

1. C.D. Gutsche, Calixarenes, Royal Society of Chemistry, Cambridge, 1989; C.D. Gutsche, Calixarenes Revisited, Royal Society of Chemistry, Cambridge, 1998.
2. Calixarenes, a versatile class of macrocyclic compounds, eds. J. Vicens, V. Bohmer, Kluwer, Dordrecht, 1991.
3. S. Shinkai, S. Mori, H. Koreishi, T. Tsubaki, O. Manabe, J. Am. Chem. Soc., 108, 1986, 2409.
4. A. Pailleret, N. Magan-Oliva, S. Ollivier, D.W.M Arrigan, J. Electroanal. Chem., under press, 2001

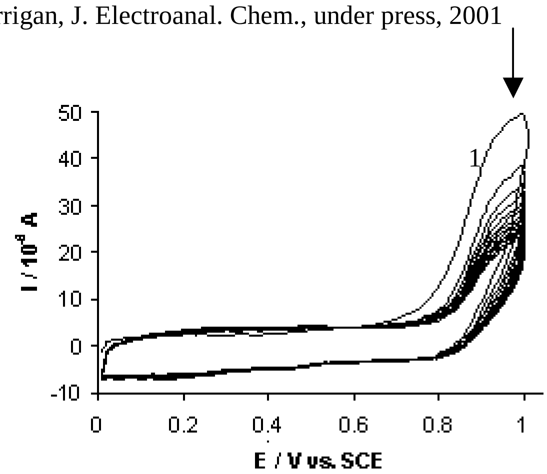


Figure 1: Electrodeposition of **1**: consecutive cyclic voltammogramms (15 scans) at a GC electrode in 0.1 M KNO_3 containing **1** (1.7 x 10^{-3} M) at pH 2. Sweep rate: 0.2 $V.s^{-1}$.

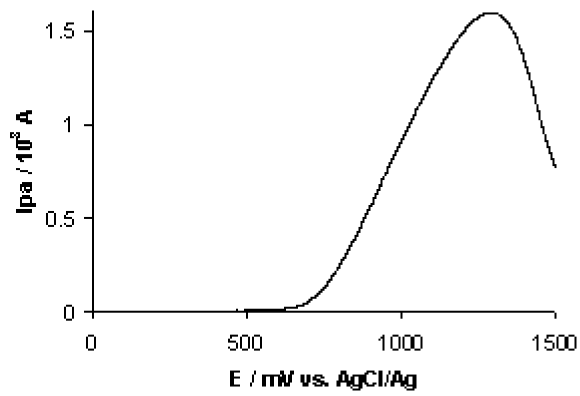


Figure 2: Adsorptive stripping voltammetry of **1** at a GC electrode in a 0.1 M KOH aqueous solution containing **1** (1.7 x 10^{-3} M) at pH 13. Sweep rate: 0.2 $V.s^{-1}$. Deposition potential: 0.25 V. Deposition time: 180 s. Quiet time: 10 s.

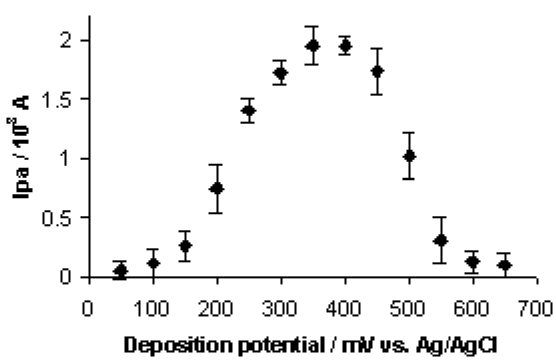


Figure 3: Variation with the deposition potential of the peak intensity measured by adsorptive stripping voltammetry of **1** at a GC electrode in 0.1 M KOH containing **1** (1.7 x 10^{-3} M) at pH 13. Sweep rate: 0.2 $V.s^{-1}$. Deposition time: 180 s. Quiet time: 10 s.